CHAPTER THREE

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The work carried out in this thesis is a comparative study between the energetics of some carbon-centered and silicon-centered free radicals. A trial has been made to represent the effect of different types of substituents on both of the stability and the geometrical structure of both radicals.

The project consists of three parts. In part one the effect of substituents on the stabilization or destabilization of the studied radicals was attempted. The effect of these substituents on the geometry of the radical was also demonstrated. In part two a conformational analysis for the selected radicals was studied. This has been done by constructing the potential energy surface of the studied radicals. While in part three the kinetics of the formation of some selected radicals were calculated. Through all the work carried out in this thesis Molecular Orbital calculations at the MNDO level with complete geometry optimization were performed.

The effect of different substituents on the stability of selected radicals was previously studied by various procedures, such as using the kinetic data, the electron spin resonance and the thermodynamical stabilization energy. In this work, that effect has been studied in terms of the

radical stabilization energy (RSE). This has been calculated from the difference in total energy between the reactants and the products in the isodesmic reactions for the radical formation. Many important and conclusive results were obtained of which,

[1] For fluoro-substituted radicals, a single fluorine atom stabilizes methyl much more than it dose with the silyl radical. This is quite clear from the radical stabilization energy of the fluoromethyl radical which equals 3.3 ev, it is much higher than that of the fluorosilyl radical which equals 0.4ev. On the other hand, di- and tri- fluoro substituted silicon centered radicals had higher RSE than the corresponding carbon-centered radicals. substitution by a fluorine atom has decreased significantly the charge density on the central atom, carbon atom in case of methyl radical. Such effect was not pronounced in case of silicon-centered radical due to the large size of silicon atom. On the other hand substitution with more than one fluorine atom leads to repulsion between fluorine atoms which is less pronounced in the case of silicon radicals (size effect).

[2] For hydroxy-substituted radicals, the,silyl substituted radicals behave almost exactly as the corresponding carbon-centered radicals. The RSE is the same for $^{\cdot}CH_2OH$ and $^{\cdot}SiH_2OH$, slightly higher for $^{\cdot}SiH(OH)_2$ than for $^{\cdot}CH(OH)_2$ and for $^{\cdot}Si(OH)_3$ than for $^{\cdot}C(OH)_3$.

[3] In case of amino-substituted silyl radicals, the RSE

increases on increasing the amino substitution and it is higher than that encountered with methyl amino substituted radicals.

[4] The captodative effect is pronounced in determining the RSE of $^{\cdot}CHF(NH_2)$ which is found to be larger than the RSE of $^{\cdot}CH_2(NH_2)$. This is due to the high electronegativity of fluorine atom which facilitates the donating properties of the amino group.

[5] The cyanomethyl and cyanosilyl radicals have the lowest RSE compared to other substituted radicals. This arises from the fact that the difference in electronegativity between carbon atom and nitrogen atom is not so pronounced and hence the electron withdrawing property of the cyano group is not significant.

A general conclusion is that, both electron-donor and electron-acceptor substituents facilitate the single-electron delocalization, lower the electron density on the radical center and adds to the stability. Hence capto-dative substituents will add extra stability.

The planar/pyramidal shapes of the studied radicals and the effect that substituents and the central atom induce in favouring one geometry over the other were investigated and discussed quantitatively on the basis of the simple MO model known as Walsh diagrams. Since this model can only predict and explain the prefered shape for the radical, the

magnitude of the induced degree of pyramidalization was calculated in different ways.

(a) By calculating $\hat{h}$, Which is the perpendicular distance between the radical center and the plane defined by three points 1.0 A° away from the radical center along the bonds of the attached atoms.

(b) By calculating the inversion barrier, which is equal to the difference in total energy between the radical in its optimized and in the planar form.

(c) By calculating the extent of interaction between the singly occupied molecular orbital and the lowest unoccupied one. Some of the conclusions drawn are :

[1] Electronegative substituents such as amino group increases the SOMO-LUMO interaction and induces the pyramidalization on the methyl radical. It also increases the pyramidalization of the silyl radical. The introduction of a second group decreases $\hat{h}$ in case of silyl radical due to steric interaction.

[2] Introduction of one hydroxy group did not affect the shape of either radicals, and pyramidalization was only induced upon the introduction of the second hydroxyl group.

[3] The successive replacement of hydrogen atoms by fluorine atoms increased the pyramidalization of the methyl and silyl radicals and in the same trend.

[4] Combination of two electronegative groups e.g. fluorine atom and amino group also increased the pyramidalization to a more extent than what had done by each substituent alone.

[5] Electronegative substituents having a Π-electron acceptor such as cyano group was found to decrease ΔE_{s-L} in case of methyl radical, but did not affect the inversion barrier or $\hat{h}$. As for the silyl radical, these substituents were predicted to decrease the pyramidalization as result of its electronic and steric effects.

[6] Introduction of an electropositive substituent such as the silyl group favoured the planar shape for methyl radical. For silyl radical $\hat{h}$ decreased considerably upon the introduction of the silyl group.

It is quite important to point out that the different substituents follow the same trend in both the carbon and the silicon series. However, the effect of the substituent which induces pyramidalization is more pronounced on silicon centered than on carbon centered radicals. This is reflected on the high $\hat{h}$ values for silicon radicals as compared with their values for carbon centered radicals.

In the second part of this work an exciplicit conformational analysis for some carbon-centered and some silicon-centered free radicals has been made. This analysis was performed by constructing a potential energy surface (PES).

The potential function $V(\phi)$ which describes the internal rotation about a single bond was calculated then was expanded as a Fourier series. This series is generally truncated after three terms (V_1, V_2 and V_3). The first term is related to the dipolar or steric interactions, the second term corresponds to the conjugative or hyperconjugative interaction, whereas V_3 is mainly dependent on the repulsion between electrons of bond pairs.

The examples studied were selected to include the most important bonds around which intramolecular rotation can occur, such as Si-Si, Si-O and Si-N bonds. The effect of captor, donor and captodative substituents on the height of the rotational barrier was investigated through using substituents as fluorine atom, amino and hydroxy groups. As the substituent rotates about a single bond of the molecule, each of the three components - resulting from the Fourier expansion - would favour one of the conformers over the others. The outcome of the competing effect of these components determines the shape of the rotational potential curve with its maxima and minima.

In all the studied cases the height of the energy barrier between any two conformers is less than 10 kcal/mol. In a sence, one can say that there is a free rotation around all the central atom-substituent bonds. Consequently, the substituted radicals can adopt many interconvertable confir-

mation in the space. But there is always one most stable conformer. The geometry of this conformer is governed by the sum of the polar and steric factors exerted by the substituent attached to the central atom. Since in all the studied examples, the substituent has one or more lone pair of electrons on the atom α- to the central atom, and this lone pair is capable of overlaping with the odd electron on the central atom as well as forming three electrons bond. Hence, these substituents exerted relatively the same stabilizing or destabilizing effect on the opposed configuration and as a result all the studied radicals were found to have a common stable conformer. Small deviation from this configuration was found. This was attributed to the difference in electronegativity of the central atoms and substituents as well as to the steric factor.

In part three of this work a kinetic study to calculate the specific rate constant for the formation of some carbon centered and some silicon centered free radicals was performed. This has been done using the transition state theory (TST) in combination with MO calculations at the MNDO level with complete geometry optimization. The activation energy as well as the best geometry of the transition state complex were calculated using the same procedures.

The kinetics of formation of the radicals were studied considering the reactions

$$AH_4 + {}^{\cdot}H \longrightarrow \left[A H_5 \right]^{\neq} \longrightarrow {}^{\cdot}AH_3 + H_2$$

[A = C or Si]

the total energy of the reactants, AH_4 and ${}^{\cdot}H$ put at 99 A° distance, and the energy of the activated complex, $AH_5^{\neq}$, in its best geometry were calculated at the MNDO level, consequently the activation energy of the reaction was obtained. The different moments of inertia as well as all the vibration frequencies of the reactants, the transition state complex and the products were calculated. The different partition functions were calculated and finally the specific rate constant for the formation of the studied radicals.

The activation energy of formation of silicon-centered free radicals were found to be much less (up to twenty times) than the activation energy of formation of carbon-centered radicals. As a result, the specific rate constants are much higher (up to four times) for the formation of silicon-centered radicals. This is attributed to the large size of silicon atom compared to that of carbon atom. This large size leads to a lower charge density on the central atom, it also leads to a longer Si-H bond than C-H bond, to a lower steric effect between the silane molecule and the attacking hydrogen atom, and consequently to a faster and less energy demanding process.

Another factor which facilitates the process of formation of silicon centered radical relative to the formation of carbon centered radical is the geometry of the formed radical. While all silicon radicals - involved in this study - are known to be pyramidal, this is not the case with carbon centered radicals. Thus the methyl radical is absolutely planar, the cyano, the amino and the hydroxy methyl radicals deviate only slightly from planarity. Accordingly, while the formation of methyl radical has the highest rate in the carbon series, the formation of silyl radical has the lowest rate in the silicon series. Except for the methyl radical, the rate of formation for the different substituted methyl and silyl radicals followed nearly the same order.